Boehmite@tryptophan-Pd nanoparticles: A new catalyst for C-C bond formation

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1 | INTRODUCTION

In recent years, with the aim of combining the advantages of homogeneous and heterogeneous catalytic processes, nanoparticles have been employed due to their high surface area and facile recovery.^[1-6] Important nano-heterogeneous supports such as metal oxides, carbon nanotubes, ionic liquids, molecular sieves (SBA-15, MCM-41 and MCM-48), alumina, peptide nanofibers, silica nanoparticles, polymers, graphene oxide and heteropoly acids have been employed for the heterogenization of homogeneous catalysts.^[7-19] Among the various supports, boehmite nanoparticles are considered as outstanding solid supports because of their physical and chemical properties such as excellent thermal and chemical stability, large internal surface area and high concentration of surface OH groups. Boehmite nanoparticles have applications in a wide variety of endeavors such as: the preparation of sol-gel ceramics,^[20] for

A boehmite@tryptophan-Pd nanoparticulate catalyst was prepared by a simple, fast and convenient route. The nanomaterial was characterized using various techniques and employed as a thermally stable catalyst for Heck, Stille and Suzuki cross-coupling reactions. Optimized conditions for these reactions are described. The catalyst could be isolated, post-reaction, by simple filtration and recycled for several consecutive cycles without a notable change in its activity.

KEYWORDS

Boehmite, Heck reaction, Stille reaction, Suzuki reaction

rheology control,^[21] as medicinal^[22] desiccants and their carrier,^[23] as absorbents,^[24] for coatings,^[25] in electrochemical sensors,^[26] as vaccine adjuvants, in the petrochemical industry^[27] and most widely used as catalysts and catalyst carriers.^[28] More importantly, the immobilization of transition metal complexes on the nano-boehmite surface has been rarely reported in the literature for the purpose of synthesizing heterogeneous catalysts.^[29–33]

L-Tryptophan is an amino acid that contains an α -amino group, an α -carboxylic acid group and a sidechain indole, making it a nonpolar aromatic amino acid.^[34] Generally speaking, the presence of an amino group beside a carboxylic acid group can accelerate the immobilization process which may be aided by the N—H group of tryptophan which is capable of forming a hydrogen bond with the O—H groups on a boehmite surface. Also, the final complex can be synthesized using stable interaction between the amine group of tryptophan and a palladium atom. It should be mentioned that tryptophan which has a natural origin was selected as an inexpensive and green ligand.

Over the past several decades, there has been growing interest in the improvement of experimental procedures for the design and synthesis of transition metal catalysts with nanoscale size. There are many reports of palladium complexes supported on the surface of various solids such as magnetic nanoparticles and mesoporous materials (MCM-41,^[35] MCM-48^[36] and SBA-15^[37]). In particular, special attention has been paid to heterogeneous palladium catalysts because of their applications in carbon-carbon bond forming reactions such as Suzuki-Miyaura,^[38] Hatanaka,^[39] Hiyama,^[40] Stille,^[41] Espinet/Echavarren^[42] and Heck and Sonogashira^[43] reactions. It should be noted that there are only few reports describing complexes supported on the surface of boehmite for C-C bond formation.^[44-46] As reported in several reviews, the use of Suzuki, Stille and Heck coupling reactions is indispensable for the synthesis of high-value chemicals such as natural products.^[47] agrochemicals,^[48] pharmaceuticals,^[49] polymers,^[50] biologically active compounds and advanced materials.^[50] These reactions benefit from the low toxicity and commercial availability of boronic acid, boronate ester derivatives or triphenyltin chloride and alkene sources.^[51-54]

In our continuing efforts towards the development of efficient, inexpensive and green catalysts for carbon– carbon bond formation reactions, we have designed a novel heterogeneous catalyst for the reactions mentioned above. Herein, we present a simple and inexpensive procedure, combining ease of operation, easy separation of the catalyst, short reaction times and high yield of products.

2 | EXPERIMENTAL

2.1 | Materials

All chemicals and solvents used in this work were obtained from Sigma-Aldrich and Merck. They were used without further purification. The particle size and morphology were examined using scanning electron microscopy (SEM) with an FESEM-TESCAN MIRA3. ¹H NMR spectra were recorded with a Bruker NMR (400 MHz) spectrometer. Powder X-ray diffraction (XRD) measurements were performed using a Philips X'pert powder X-ray diffractometer (Cu K α radiation, $\lambda = 1.54060$ Å). Fourier transform infrared (FT-IR) spectra of samples were recorded with KBr pellets using a Bruker VRTEX 70 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) curves were obtained with a Shimadzu DTG-60 instrument. Melting points were obtained using an Electrothermal 9100 apparatus. The content of Pd was measured using inductively coupled plasma optical emission spectrometry (ICP-OES).

2.2 | Preparation of L-tryptophan complex of Pd supported on surface of boehmite nanoparticles (boehmite@tryptophan-Pd)

Boehmite nanoparticles were prepared by the sol-gel method as reported in our previous work.^[15] For the synthesis of L-tryptophan supported on boehmite nanoparticles, 1 g of the prepared boehmite nanoparticles was dispersed in 50 ml of deionized water by sonication for 15 min, and then L-tryptophan (2.5 mmol) was added to the mixture. The reaction mixture was stirred under nitrogen atmosphere at reflux conditions for 24 h. Then, the obtained boehmite@tryptophan product was separated by simple filtration and washed with hot water and hot ethanol to remove the unreacted amino acid and dried in an oven at 50°C for 4 h. The obtained boehmite@tryptophan (0.5 g) was dispersed in 25 ml of ethanol by sonication for 30 min and then palladium acetate (0.25 g) was added to the reaction mixture. The reaction mixture was stirred under nitrogen atmosphere at 80°C for 24 h. Then, 3 mmol of NaBH₄ was added to the reaction and stirred for a further 2 h. The final product (boehmite@tryptophan-Pd) was separated by simple filtration and washed with ethanol to remove the unattached substrates. The boehmite@tryptophan-Pd nanoparticulate product was dried in an oven at 50°C for 4 h.

2.3 | General procedure for Suzuki reaction

A mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol) and Na_2CO_3 (1.5 mmol) was dissolved in 2 ml of ethanol. Boehmite@tryptophan-Pd (0.075 mol%) was added to the mixture, and the flask was sealed and stirred at 70°C. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature and the catalyst was separated by simple filtration and washed with EtOAc. Finally, the reaction mixture was dried over Na_2SO_4 . Finally, the solvent was evaporated, and the pure biphenyl derivative was obtained.

2.4 | General procedure for Stille reaction

A mixture of aryl halide (1 mmol), triphenyltin chloride (0.5 mmol) and Na_2CO_3 (1.5 mmol) was dissolved in



SCHEME 1 Synthesis of boehmite@tryptophan-Pd nanoparticles

2 ml of ethanol. Boehmite@tryptophan-Pd (0.075 mol%) was added to the flask and the reaction vessel was sealed and stirred at 70°C. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature, and the catalyst was separated by simple filtration and washed with EtOAc. The reaction mixture was then extracted with water and EtOAc. The organic layer was dried over Na₂SO₄. The solvent was evaporated, and pure biphenyl derivative was obtained in good yield.

2.5 | General procedure for Heck reaction

A mixture of aryl halide (1 mmol), butyl acrylate (1.2 mmol) and K_2CO_3 (3 mmol) was dissolved in 2 ml of dimethylsulfoxide (DMSO). Boehmite@tryptophan-Pd (0.105 mol%) was added to the flask, and the mixture



FIGURE 1 FT-IR spectra of (a) boehmite, (b) boehmite@tryptophan and (c) boehmite@tryptophan-Pd

was stirred at 120°C. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature, and the catalyst was separated by simple filtration and washed with Et₂O. The reaction mixture was extracted with water and Et₂O. The organic layer was dried over Na₂SO₄. The solvent was then evaporated, and the corresponding pure productwas obtained.



FIGURE 2 EDX analysis of boehmite@tryptophan-Pd

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2.6 | Selected spectral data

1,1'-Biphenyl (Table 2, entry 1). ¹H NMR (400 MHz, CDCl₃, $\delta_{\rm H}$, ppm): 7.67–7.59 (m, 4H), 7.53–7.42 (m, 4H), 7.42–7.34 (m, 2H).

4-Methyl-1,1'-biphenyl (Table 2, entry 6). ¹H NMR (400 MHz, CDCl₃, $\delta_{\rm H}$, ppm): 7.64–7.60 (m, 2H), 7.54–7.52 (m, 2H), 7.50–7.44 (m, 2H), 7.39–7.33 (m, 1H), 7.30–7.28 (m, 2H), 2.43 (s, 3H).

4-Methoxy-1,1'-biphenyl (Table 3, entry 3). ¹H NMR (400 MHz, CDCl₃, $\delta_{\rm H}$, ppm): 7.60–7.54 (m, 4H), 7.48–7.46 (m, 2H), 7.36–7.30 (m, 1H), 7.03–6.98 (m, 2H), 3.88 (s, 3H).



FIGURE 3 XRD pattern of boehmite@tryptophan-Pd nanocatalyst

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4-Nitro-1,1'-biphenyl (Table 2, entry 8). ¹³C NMR (101 MHz, CDCl₃, δ_C, ppm):147.63, 147.08, 138.76, 129.16, 128.93, 127.80, 127.47, 127.39, 124.11.

Butyl cinnamate (Table 5, entry 1). ¹H NMR (400 MHz, CDCl₃, $\delta_{\rm H}$, ppm): 7.73–7.69 (d, J = 16.0 Hz, 1H), 7.56–7.53 (m, 2H), 7.42–7.38 (m, 3H), 6.49–6.45 (d, J = 16.0 Hz, 1H), 4.24 (t, J = 6.7 Hz, 2H), 1.74–1.68 (m, 2H), 1.51–1.42 (m, 2H), 1.01–0.97 (t, J = 7.4 Hz, 3H).

Butyl 3-(4-methoxyphenyl)acrylate (Table 5, entry 3). ¹H NMR (400 MHz, CDCl₃, $\delta_{\rm H}$, ppm): 7.68 (d, J = 16.0 Hz, 1H), 7.45–7.43 (m, 2H), 7.22–7.20 (m, 2H), 6.42 (d, J = 16.0 Hz, 1H), 4.23 (t, J = 6.7 Hz, 2H), 1.71 (m, 2H), 1.51–1.42 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

3 | RESULTS AND DISCUSSION

3.1 | Catalyst preparation

Previously, we reported the synthesis of a heterogeneous nanocatalyst by simple procedures and available materials, the catalyst being applicable in the Heck, Stille and Suzuki coupling reactions.^[55–57] As illustrated in Scheme 1, the synthesis of the new heterogeneous nanocatalyst was realized by attaching tryptophan to the boehmite nanosubstrate. Ultimately, boehmite@tryptophan-Pd nanocatalyst was prepared using the stable interaction between the nitrogen atom (primary amine) of tryptophan and palladium (Scheme 1).



FIGURE 4 X-ray mapping analysis of boehmite@tryptophan-Pd nanocatalyst

3.2 | Catalyst characterization

The prepared heterogeneous catalyst was characterized using FT-IR spectroscopy, SEM, energy-dispersive X-ray spectroscopy (EDX), XRD, TGA and X-ray mapping.

The FT-IR spectra of boehmite, boehmite@tryptophan and boehmite@tryptophan-Pd are shown in Figure 1. In the FT-IR spectrum of the boehmite nanoparticles, two strong bands at 3086 cm⁻¹ (symmetric mode) and 3295 cm⁻¹ (asymmetric mode) are attributed to the O–H bonds on the surface of boehmite nanoparticles.

In all the FT-IR spectra, several peaks at 480, 618 and 743 cm⁻¹ were observed that are related to the absorption of Al–O bonds.^[58] In the spectrum of boehmite@tryptophan (Figure 1b), the peaks at around 1615 and 2842–2946 cm⁻¹ are the most important, characteristic of the stretching vibrations of aromatic C=N bond and aliphatic C–H stretching vibration, respectively. More importantly, the bending vibration of NH₂ near 1450 cm⁻¹ in the FT-IR spectrum of boehmite@tryptophan is shifted to lower wavenumber in the spectrum of boehmite@tryptophan-Pd (Figure 1



FIGURE 5 SEM images of boehmite@tryptophan-Pd nanocatalyst at different magnifications



FIGURE 6 TGA curves of boehmite@tryptophan-Pd nanocatalyst

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c), confirming the coordination of nitrogen atom of

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amino groups to palladium. In order determine the elemental composition of the boehmite@tryptophan-Pd nanocatalyst, the components were analyzed using EDX (Figure 2). The elements Al, O, C, N and Pd were observed in the EDX analysis of boehmite@tryptophan-Pd. In order to determine the exact amount of palladium, the ICP-OES technique was

applied. According to the ICP-OES results, the exact

amount of Pd in this catalyst is 1.52×10^{-3} mol g⁻¹. Also,

in order to determine the amounts of carbon and nitrogen in the catalyst, elemental analysis was performed. According to this analysis, the amount of carbon and nitrogen immobilized on boehmite nanoparticles was 13.2 and 2.8%, respectively.

The XRD pattern of the boehmite@tryptophan-Pd nanocatalyst is shown in Figure 3. The peaks at 2θ values of 14.01°, 18.54°, 20.13°, 24.95°, 28.95°, 41.45°, 47.25°, 53.24°, 55.22°, 59.12°, 64.24° and 68.26° are related to (0 2 0), (1 2 0), (0 3 1), (1 3 1), (0 5 1), (2 0



SCHEME 2 Carbon–carbon coupling reactions in the presence of boehmite@tryptophan-Pd

TABLE I Optimization of reaction conditions for C=C cross-coupling of fouroutizence with phenyboronic a	TABLE 1	Optimization of reaction	conditions for C-C	cross-coupling of iodobenze	ene with phenylboronic acid
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Entry	Catalyst (mol%)	Solvent	Base	Temperature (°C)	Time (min)	Yield (%) ^a
1	_	EtOH	Na ₂ CO ₃	70	600	NR
2	0.015	EtOH	Na ₂ CO ₃	70	30	62
3	0.045	EtOH	Na ₂ CO ₃	70	30	80
4	0.075	EtOH	Na ₂ CO ₃	70	30	98
5	0.105	EtOH	Na ₂ CO ₃	70	30	98
6	0.135	EtOH	Na ₂ CO ₃	70	30	93
7	0.075	DMF	Na ₂ CO ₃	70	30	92
8	0.075	H_2O	Na ₂ CO ₃	70	30	45
9	0.075	PEG	Na ₂ CO ₃	70	30	94
10	0.075	EtOH	КОН	70	30	85
11	0.075	EtOH	K ₂ CO ₃	70	30	82
12	0.075	EtOH	NaOH	70	30	77
13	0.075	EtOH	Et ₃ N	70	30	95
14	0.075	DMSO	Na ₂ CO ₃	70	30	87
15	0.075	EtOH	—	70	320	b
16	0.075	EtOH	Na ₂ CO ₃	Reflux	30	97
17	0.075	EtOH	Na ₂ CO ₃	65	30	62
18	0.075	EtOH	Na ₂ CO ₃	40	30	46
19	0.075	EtOH	Na ₂ CO ₃	25	360	NR

^aIsolated yield.

^bReaction conditions: aryl halide (1 mmol), boehmite@tryptophan-Pd, phenylboronic acid (1 mmol), base (1.5 mmol) and solvent (2 ml).

TABLE 2 Catalytic C-C coupling reaction of aryl halides using $PhB(OH)_2$ in the presence of catalytic amounts ofboehmite@tryptophan-Pd in EtOH at 70°C

Entry	Aryl halide	Product	Time (min)	Yield (%) ^a
1			30	98
2	Me	Me	55	96
3	MeO	MeO	40	97
4			70	82
5	Br	$\bigcirc - \bigcirc \bigcirc$	45	91
6	Me	Me	70	92
7	NC Br		55	96
8	Br	MeO	110	88
9	GF ₃	F ₃ C	120	81
10	CI	ci	60	93
11	O ₂ N Br	0 ₂ N-	30	98
12	CI	$\bigcirc - \bigcirc \bigcirc$	120	88
13	O ₂ N	0 ₂ N	100	91
14	H ₂ N	H ₂ N	230	86
15	NC		160	91
16	HO	но-	195	87
17	Ac	Ac-	220	92

^aIsolated yield.

 bReaction conditions: aryl halide (1 mmol), boehmite@tryptophan-Pd (0.075 mol %), phenylboronic acid (1 mmol) and Na_2CO_3 (1.5 mmol) in EtOH at 70°C.

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0), (1 5 1), (0 8 0), (2 3 1), (0 0 2), (1 7 1) and (2 5 1) reflections, respectively, which are in agreement with the standard boehmite XRD pattern.^[59] More importantly, the phase of boehmite is not destroyed during the modifications.

The X-ray mapping of the boehmite@tryptophan-Pd nanocatalyst is shown in Figure 4. The good dispersion of Pd on the surface of the catalyst was confirmed from the elemental mapping images.

To investigate the size and morphology of the boehmite@tryptophan-Pd nanocatalyst, SEM images were obtained (Figure 5). The images show that most of

TABLE 3 Coupling of aryl halides with Ph_3SnCl in the presenceof catalytic amounts of boehmite@tryptophan-Pd in EtOH at 70°C

Entry	Aryl halide	Product	Time (min)	Yield (%) ^a
1			50	96
2	Me	Me	95	93
3	MeO	MeO	80	94
4	U OMe		180	87
5	Br	$\bigcirc - \bigcirc \bigcirc$	95	91
6	Me	Me	150	90
7	NC Br		110	93
8	Br	MeO	180	85
9	Br CF ₃	F ₃ C	210	77
10	CI	ci	140	92
11	O ₂ N Br	0 ₂ N-	135	94
12	O ₂ N CI	0 ₂ N-	100	78

^aIsolated yield.

^bReaction conditions: aryl halide (1 mmol), boehmite@tryptophan-Pd (0.075 mol %), triphenyltin chloride (0.5 mmol) and Na_2CO_3 (1.5 mmol) in EtOH at 70°C.

the boehmite@tryptophan-Pd nanoparticles are quite homogeneous with an average size in the region of 62 nm.

The immobilization of tryptophan-Pd complex on the surface of boehmite was also confirmed by TGA (Figure 6). It should be mentioned that the weight loss below 200°C may be due to the removal of the physically and chemically adsorbed solvents or surface hydroxyl groups. The weight loss between 200 and 500°C is due to the decomposition of organic groups on the surface of boehmite.^[58]

3.3 | Catalytic studies

As a part of the present research, it was decided to consider the catalytic activity of boehmite@tryptophan-Pd in some organic reactions including the synthesis of biphenyl and butyl cinnamate derivatives (Scheme 2).

A reaction optimization study was undertaken wherein the amount of catalyst, type of solvent and base and also the effect of temperature were investigated via the reaction of iodobenzene (1 mmol) with phenylboronic acid (1 mmol). The results are summarized in Table 1. According to the observed results, conditions for the optimal this reaction are: aryl halide (1 mmol), phenylboronic acid (1 mmol), boehmite@tryptophan-Pd (5 mg) and Na₂CO₃ (1.5 mmol) in ethanol at 70 C (Table 1, entry 4).

In order to investigate the scope and generality of this procedure, various types of aryl halides were reacted with phenyl donors including phenylboronic acid and triphenyltin chloride under the optimized conditions. The results are summarized in Tables 2 and 3. The experimental results show that various *ortho-*, *meta*- and *para*-substituted aryl halides including aryl iodides, aryl bromides and aryl chlorides having both electron-



SCHEME 3 Boehmite@tryptophan-Pdcatalyzed Heck reaction

Entry	Catalyst (mg)	Solvent	Base	Temperature (°C)	Time (min)	Yield (%) ^a
1	_	DMSO	K ₂ CO ₃	120	One day	NR
2	0.015	DMSO	K ₂ CO ₃	120	85	45
3	0.030	DMSO	K_2CO_3	120	85	68
4	0.075	DMSO	K ₂ CO ₃	120	85	87
5	0.105	DMSO	K ₂ CO ₃	120	85	95
6	0.105	PEG	K ₂ CO ₃	120	85	68
7	0.105	DMF	K ₂ CO ₃	120	85	87
8	0.105	Toluene	K ₂ CO ₃	120	85	41
9	0.105	EtOH	K ₂ CO ₃	120	85	86
10	0.105	H ₂ O	K ₂ CO ₃	120	85	Trace
11	0.105	DMSO	Et ₃ N	120	85	83
12	0.105	DMSO	КОН	120	85	37
13	0.105	DMSO	NaOH	120	85	46
14	0.105	DMSO	Na ₂ CO ₃	120	85	85
15	0.105	DMSO	_	120	500	NR
16	0.105	DMSO	K ₂ CO ₃	r.t	85	Trace
17	0.105	DMSO	K ₂ CO ₃	80	85	55
18	0.105	DMSO	K ₂ CO ₃	100	85	71
19	0.105	DMSO	K ₂ CO ₃	110	85	84
20	0.105	DMSO	K ₂ CO ₃	130	85	96

TABLE 4 Optimization of reaction conditions for C-C coupling reaction of iodobenzene with butyl acrylate

^aIsolated yield.

^bReaction conditions: aryl halide (1 mmol), boehmite@tryptophan-Pd, butyl acrylate (1.2 mmol), base (3 mmol) and solvent (2 ml).

TABLE 5Coupling of aryl halides with butyl acrylate in thepresence of catalytic amounts of boehmite@tryptophan-Pd



^aIsolated yield.

 bReaction conditions: aryl halide (1 mmol), boehmite@tryptophan-Pd (0.105 mol%), butyl acrylate (1.2 mmol) and K_2CO_3 (3 mmol) in DMSO at 120°C.

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withdrawing and electron-donating groups produced their corresponding biphenyl derivatives in good to excellent yields. However, it is worth mentioning that the reaction time for aryl halides with electron-donating groups on the aromatic ring was longer than that for aryl halides with electron-withdrawing groups. In order to investigate the chemoselectivity of this new catalytic system, the reaction of 1-bromo-4-chlorobenzene was also investigated in which the bromide showed more reactivity (Tables 2 and 3, entry 10). This selectivity allows an active halide site to remain for further functionalization.

In the next experiment, the catalytic activity of boehmite@tryptophan-Pd for the Heck reaction was examined (Scheme 3). For this purpose, the C-C crosscoupling reaction between iodobenzene and butyl acrylate, in the presence of boehmite@tryptophan-Pd, was considered as a model reaction and performed under conditions of various solvents and amounts of the catalyst to elucidate the best reaction conditions (Table 4). Initially, the effect of the amount of catalyst on the reaction was studied, and this revealed that the highest vield of product was obtained in the presence of 7 mg of boehmite@tryptophan-Pd. Meanwhile, in the absence of the catalyst, the reaction did not proceed at all even after 24 h (Table 4, entry 1). In the next step, the effect of solvent was investigated, and the best result was obtained with DMSO. Then, the effect of various bases was investigated and K₂CO₃ was selected as the most effective base. Also, the effect of the temperature was studied, with the highest yield of product being obtained at 120°C (Table 4, entries 9 and 10).

With the optimal conditions in hand, a variety of aryl halides bearing various functional groups were examined. The results presented in Table 5 show that the boehmite@tryptophan-Pd catalytic system worked very well, and various types of aryl halides exhibited good reactivities and the corresponding butyl cinnamate derivatives were obtained in excellent yields.

3.4 | Recyclability of catalyst

The reusability of a heterogeneous catalyst is an important factor from an industrial point of view. Thus, the recyclability of boehmite@tryptophan-Pd was examined via the Heck cross-coupling reaction. After completion of the reaction, the mixture was cooled to room temperature, the catalyst was separated by simple filtration from the reaction mixture and the filtered catalyst was washed with CH_2Cl_2 and EtOAc and then with hot doubly distilled water several times. Afterwards, the recovered catalyst from the model reaction was dried in an oven 10 of 11 WILEY-Organometallic

at 120°C for 4 h and was reused in the next run. This catalyst was recycled and reused over five times without significant loss of its catalytic activity (Figure 7).

3.5 | Leaching study

In order to determine the leaching of palladium into reaction media, ICP-OES analysis was performed. The palladium content in reaction media in the synthesis of 1,1'biphenyl (Suzuki reaction), 4-methoxy-1,1'-biphenyl (Stille reaction) and butyl cinnamate (Heck reaction) was found to be 0.72, 0.85 and 1.11%, respectively. The results show that the leaching of palladium into reaction media is negligible.

3.6 | Hot filtration test

Also, the heterogeneity of boehmite@tryptophan-Pd in the reaction mixture was studied using the hot filtration test. The hot filtration test was performed in Heck cross-coupling reaction as the model reaction under the optimal reaction conditions. After 43 min (half the reaction time), the reaction was terminated, and corresponding product obtained in 55% yield. Then, the reaction was repeated, and at half the reaction time, the catalyst was separated by simple filtration from the reaction mixture and the filtrate was allowed to react further (in the absence of catalyst). We found that only a trace conversion (<6%) of the coupling reaction was observed upon heating of the catalyst-free solution for another 43 min.

4 | CONCLUSIONS

Boehmite nanoparticles were easily synthesized and coated with tryptophan via covalent cross-linking to make



FIGURE 7 Recyclability study (reaction conditions: iodobenzene (1 mmol), butyl acrylate (1.1 mmol), base (3 mmol), boehmite@tryptophan-Pd (0.105 mol%), 120°C, 85 min)

an efficient support for palladium. The catalytic activity of this nanostructural material was investigated in the Suzuki, Stille and Heck C–C cross-coupling reactions. Our reported procedure offers the outstanding benefits of excellent yields and green reaction conditions, easy catalyst preparation, use of inexpensive and available materials, short reaction times, easy separation, catalyst recyclability and high catalyst chemical stability.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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